

**United States Department of Agriculture  
Agricultural Marketing Service, Science & Technology  
Pesticide Data Program**

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Title: Analytical Reference Standards		
Revision: 1	Replaces: 01/01/08	Effective: 07/01/08

**1. Purpose:**

To provide standard procedures for analytical standards used in the USDA/AMS Pesticide Data Program (PDP).

**2. Scope:**

This standard operating procedure (SOP) shall be followed by all laboratories conducting residue studies for PDP, including support laboratories conducting stability or other types of studies that may impact the program.

**3. Outline of Procedures:**

- 5.1 Ordering Analytical Standards
- 5.2 Receipt of Analytical Standards
- 5.3 Storage of Analytical Standards
- 5.4 Preparation of Stock Solutions
- 5.5 Preparation of Intermediate Dilutions
- 5.6 Standard Checking
- 5.7 Expired Standard Verification
- 5.8 Working Dilutions/Mixed Standards
- 5.9 Detector Profiles
- 5.10 Disposal of Analytical Standards

**4. References:**

- USDA/AMS PDP Quality Assurance/Technical Meeting, March 20-22, 2007, Crystal City, VA
  - 40 CFR 160.47, Facilities for handling test, control, and reference substances
  - 40 CFR 160.83, Reagents and Solutions
  - 40 CFR 160.105, Test, control and reference substance characterization
  - 40 CFR 160.107, Test, control, and reference substance handling
  - 40 CFR 160.113, Mixtures of substances with carriers
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- de Kok et. al., The Stability of Pesticide Standards and Solutions, 5<sup>th</sup> European Pesticide Residue Workshop, Stockholm, Sweden, June 13-16, 2004
- Avramides, The Stability of Pure Standards and Stock Standard Solutions for Pesticide Residue Determination Using Gas Chromatography, 5<sup>th</sup> European Pesticide Residue Workshop, Stockholm, Sweden, June 13-16, 2004
- Vieth et. al, Storage Stability of Stock Solutions and Solid Pesticide Standards, 5<sup>th</sup> European Pesticide Residue Workshop, Stockholm, Sweden, June 13-16, 2004

**5. Specific Procedures:**

This SOP represents minimum PDP requirements and is presented as a general guideline. Each laboratory shall have written procedures that provide specific details concerning how the procedure has been implemented in that laboratory.

**5.1 Ordering Analytical Standards**

**5.1.a** Analytical standards are available under blanket purchasing agreements established with approved PDP vendors. USDA Manassas may be contacted to order standards on individual laboratory accounts.

**5.1.b** Standards may also be obtained from the EPA Repository or requested from registrants. The EPA repository is located at:

EPA National Pesticide Standard Repository  
Environmental Science Center  
701 Mapes Road  
Fort Meade, MD 20755-5350  
Phone: (410)305-2931  
FAX: (410) 305-2999  
[http://www.epa.gov/oppbead1/labs/standards\\_repository.htm](http://www.epa.gov/oppbead1/labs/standards_repository.htm)

**5.1.c** Procurement of standards from all sources must meet the following minimum requirements:

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A current and valid “Certificate of Analysis” (CoA) is available (as a minimum requirement the certification shall identify the substance, its purity, and the production lot), traceability, and current expiration date.

**Note1:** *An exemption for CoA and current expiration date is allowed for extraneous environmental contaminants aldrin, BHC, chlordane, DDT (and metabolites), dieldrin, endrin, heptachlor (and metabolite), and lindane that are covered by FDA Action Levels.*

**Note 2:** *For all other analytical standards, in some cases, a current and valid CoA may not accompany the analytical standard. In this case, the laboratory shall contact the vendor to determine if one is available; if one is not available, the laboratory is exempt from the requirement to maintain a current and valid CoA for that standard.*

## **5.2 Receipt of Analytical Standards**

Custody of a standard begins when the standard is received in the laboratory. Each standard shall be given a code which shall uniquely identify the standard from neat material to final dilutions. Receipt of standards shall be documented and each standard shall be traceable. Records shall include name, unique code, purity, lot number, date received, and expiration date (see note in 5.1.c for exemption).

## **5.3 Storage of Analytical Standards**

**5.3.a** Neat standards shall be kept in a separate standards freezer, preferably at approximately -20°C or lower unless degradation occurs at such temperatures. In these cases, neat standards shall be stored at the recommended temperature.

**5.3.b** Stock standards and dilutions including mixed standards shall be kept in refrigerators or freezers separate from those used for samples or reagents. Stock standards and dilutions shall be stored in teflon-lined, screw-capped, glass bottles or sealed glass ampules.

**5.3.c** Access to the freezers and refrigerators shall be controlled and standards usage documented through the use of appropriate records (e.g., log books). These records shall contain at a minimum: standard name and/or unique code, date and time removed, initials of person removing standard, date and time returned, initials of person returning standard.

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**5.3.d** Refrigerator and freezer temperatures shall be checked either by taking readings each working day, or by automatic temperature recording devices.

#### **5.4 Preparation of Stock Standard Solutions**

Stock standard solutions shall be prepared in a separate standard preparation area to avoid contamination of samples with pesticide standards. Each stock standard shall be given a unique identifying code and shall be labeled with a minimum of: pesticide name, concentration, solvent, date of preparation, initials of preparer, and expiration date of solution. Written SOPs for stock standard preparation shall include the method for preparing standards, calculations used in standard preparation, documentation which provides for standard traceability and safety guidelines. Data recorded for each neat source standard shall include source, lot number, date received, expiration date, purity, and amount used.

#### **5.5 Preparation of Intermediate Dilutions**

Intermediate dilutions, including mixed standards, shall be prepared in a separate standard preparation area. Each standard shall be given a unique identifying code and shall be labeled with pesticide name, concentration, solvent, date of preparation, initials of preparer, and expiration date of solutions. Written SOPs shall include the method for standard preparation and documentation which provides for standard traceability.

#### **5.6 Standard Checking**

**5.6.a** Stock solutions of neat pesticide standards not previously prepared or not currently in use in the laboratory shall be prepared in duplicate and the two standards compared to each other. Responses for standards of comparable concentrations must match within 10% relative percent difference (RPD):

$$RPD = \frac{|RF_1 - RF_2|}{[(RF_1 + RF_2)/2]} \times 100,$$

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where  $RF_1$  is the response factor<sup>1</sup> of the first analytical standard and  $RF_2$  is the response factor of the second standard. If standards do not match, a third standard shall be made and compared. This process shall be continued until two matching standards are prepared.

**5.6.b** New stock solutions which are prepared from neat pesticides currently used in the laboratory shall be compared to the old stock solution. The two standards must match within 10% RPD . If the two standards do not match, the problem must be identified and solved before the standard is used for quantitation. A suggested approach is to make new dilutions of both the old and new standards to check for dilution errors. If no dilution errors are found, a second stock dilution should be made to determine whether an error was made in the original preparation from neat material. If these two stocks match, then the standard may be used. If they do not match, a third stock solution should be made. Whenever possible, duplicate injections shall be used.

**5.6.c** Documentation of the standard checking process shall be kept through appropriate logbooks or electronic logs. Chromatograms of all standards shall be kept indicating the standard comparisons of old and new standards and the calculated difference.

## **5.7 Expired Standard Verification**

If a laboratory has an expired neat analytical standard and cannot obtain a replacement with a valid expiration date from an approved PDP vendor or the EPA National Pesticide Standard Repository, with a deviation from MPO on file, the laboratory may proceed with validation and analysis of samples using the expired standard under the following conditions:

**5.7.a** If the standard is recertified by the vendor and new documentation is obtained, it shall be recorded in the laboratory's standard records.

**5.7.b** If the standard is not recertified, it shall be compared to an unexpired neat when one is available to verify its integrity.

**5.7.c** If the two standards' response factors are within 10 percent, the expired standard being used shall be considered fit for purpose and this data shall be recorded in the laboratory's records.

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<sup>1</sup> Area or height of each standard divided by the concentration of that standard

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**5.7.d** If the two standards' response factors are not within 10 percent, MPO shall be contacted.

**5.7.d.1** If there residues, MPO and the laboratory's TPM and QAO shall develop an agreement on how to proceed with samples containing residues (e.g., re-extract and analyze with unexpired standard, code data as estimates, change to "unable to analyze," etc.). The agreement shall be documented and recorded in the laboratory's records. MPO will update any transmitted data in the MPO database.

**5.7.d.2** If there are non-detects and the expired standard produces a response less than the response of the unexpired standard, the LOD shall be raised (consult with MPO to determine the level) and this information shall be recorded in the laboratory's records. MPO will update any transmitted data in the MPO database. The expired standard being used shall be considered fit for purpose for qualitative analysis only and this declaration shall be recorded in the laboratory's records.

**5.8 Working Dilutions/Mixed Standards**

**5.8.a** Working dilutions and mixed standards shall be checked to ensure integrity of the solutions. These solutions should be made as frequently as necessary to ensure that concentrations do not change and/or individual pesticides do not degrade. Each laboratory shall determine the frequency of remaking dilutions/mixed standards. Documentation supporting this decision shall be kept in the form of logbooks and standard chromatograms. A suggested guideline is six months for stock mixed standards and one month for working dilutions. Some pesticides may require more frequent dilution from the stock.

**5.8.b** An archive file of all old mixed standards shall be kept and the dates the standards were used shall be indicated. The archive file shall be maintained a minimum of five years.

**5.8.c** All working solutions shall be labeled with pesticide name, solvent, date of preparation of stock, date of preparation of dilution, expiration date, and initials of preparer. Each standard shall be identified by a unique and traceable code. Mixed working standards may be coded as long as complete documentation is maintained in a logbook.

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## **5.9 Detector Profiles**

Standard retention time and response shall be characterized by analysis on the detectors used in each laboratory. These include but are not limited to: GC-ECD, GC-FPD, GC-ELCD, GC-XSD, GC-MSD, GC-ITD, LC-MS, and tandem MS. Libraries of all standards shall be developed for confirmatory instruments (GC-MS and LC-MS systems).

## **5.10 Disposal of Analytical Standards**

Each laboratory shall establish the proper procedures for disposal (e.g., disposal by a licensed contractor) of expired analytical standards (both neat standards and dilutions). Disposal shall be in accordance with the laboratory's Chemical Hygiene Plan and shall be documented.

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Revised By: Chris Pappas  
PDP Document Control Officer, Monitoring Programs Office  
8609 Sudley Road, Suite 206  
Manassas, VA 20110  
(703) 330-2300

Reviewed By: Gail Parker  
Presiding Member of PDP Technical Advisory Group  
Colorado Department of Agriculture and Consumer Services  
Chemical Residue Laboratory  
3125 Conner Boulevard, Building 3  
Tallahassee, FL 32399-1650  
(850) 410-3057

Approved By: Diana Haynes  
PDP Technical Director, Monitoring Programs Office  
8609 Sudley Road, Suite 206  
Manassas, VA 20110  
(703) 330-2300

Approved By: Martha Lamont  
PDP Administrative Program Director, Monitoring Programs Office  
8609 Sudley Road, Suite 206  
Manassas, VA 20110  
(703) 330-2300



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Revision 1	May 2008	Monitoring Programs Office
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- Deleted Section 5.2, Standard Characterization and renumbered remaining sections
- Specified approximate temperature in Section 5.4.a
- Added expired standard verification procedures to Section 5.8 and renumbered remaining sections

Original

- Combined all PDP analytical reference standard requirements into a single document
  - Added CoA exemption clause to Subsection 5.1.c
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